# Articles

## Ancillary Ligand and Ketone Substituent Effects on the Rate of Ketone Insertion into Zr-C Bonds of Zirconocene-1-Aza-1,3-diene Complexes

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Zirconocene-1-aza-1,3-diene complexes,  $[Me_2Si(C_5H_4)_2]Zr[N(Ar)CH=CHCH(Ph)]$  (Ar = Ph, **2a**; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, **2b**) and Cp<sub>2</sub>Zr[N(Ar)CH=CHCH(Ph)] (Ar = Ph, **3a**; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, **3b**), have been synthesized and characterized by NMR spectroscopy. X-ray crystal structure determinations of compounds **2a** and **3a**,**b** reveal folded five-membered-ring moieties for the zirconacycles. DFT calculations and variable-temperature NMR experiments for complex **2a** establish a rapid ring-flipping process at room temperature, with the conformation bearing a pseudoequatorial Ph group more stable by 5.6 kcal/mol. Kinetic studies on ketone insertion into these zirconocene complexes show second-order reactions, and the insertion is more favorable in the presence of a [Me<sub>2</sub>Si] *ansa* bridge, a less electron-rich substituent on the nitrogen, and a more basic ketone. One of the insertion products, namely Cp<sub>2</sub>Zr-[N(Ph)CH=CHCH(Ph)CPh<sub>2</sub>O] (**5a**), has also been characterized by X-ray crystallography.

### Introduction

Zirconocene complexes, particularly those derived from ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>ZrX<sub>2</sub>, play important roles in transition-metal-catalyzed and -promoted reactions.<sup>1</sup> One notable feature of these complexes is their ability to reverse the polarity (or induce reactivity umpolung) of carbon chains,<sup>2</sup> which is typically imposed by heteroatoms such as oxygen and nitrogen.<sup>3</sup> In the case of an  $\alpha,\beta$ -unsaturated imine, the electrophilic  $\beta$ -carbon becomes nucleophilic upon formation of a five-membered zirconacycle (Scheme 1). Evidently, the electropositive zirconium outweighs the influence of nitrogen, and the zirconocene-1-aza-1,3-diene complexes (or azazirconacyclopentenes) can be viewed as homoenolate equivalents. Such an umpolung strategy has been successfully used in the synthesis of various N-substituted pyrroles<sup>4</sup> and oxygen-containing heterocycles.<sup>5</sup> However, broader applications of this synthetic methodology are hampered by the limited electrophiles that are available for insertion into Zr-C

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bonds of the zirconacycles; only isocyanides<sup>4</sup> and ketones<sup>5,6</sup> have been identified as viable substrates for insertion.

One advantage of using transition-metal complexes for organic synthesis is that the reactivity of metal reagents can be easily modulated by altering ancillary ligands. Recent studies have shown that the incorporation of an *ansa* bridge may increase the reactivity of metallocenes by creating a more Lewis acidic metal center and providing a more spacious coordination site.<sup>7</sup> However, quantitative data explaining the enhanced

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Figure 1. Four possible stereoisomers for complex 2a.

reactivity in well-defined systems are scarce in the literature. The Parkin group has shown that rotation of the Zr–Ph bond in [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>]ZrPh<sub>2</sub> is about 400 times faster than that of Cp\*<sub>2</sub>ZrPh<sub>2</sub>.<sup>7b</sup> Their studies on H<sub>2</sub> elimination from {[Me<sub>2</sub>Si-(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>]Mo( $\eta^2$ -H<sub>2</sub>)(H)}<sup>+</sup> and [Cp\*<sub>2</sub>MoH<sub>3</sub>]<sup>+</sup> have also suggested that the [Me<sub>2</sub>Si] *ansa* bridge facilitates the elimination by a factor of ~300 in rate constant.<sup>7c</sup> For nonunimolecular processes, direct rate comparisons between *ansa*-bridged and unbridged Cp systems are even less known. Quijada, DuPont, and co-workers have reported that the overall rate of ethylene polymerization by [Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]ZrCl<sub>2</sub>/MAO (MAO = methylalumoxane) is slightly faster than the catalytic reaction with Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO;<sup>8</sup> however, no detailed kinetic study has been conducted to further address the *ansa* effect.

Zirconocene–1-aza-1,3-diene complexes bearing an *ansa* bridge may be more likely to react with electrophiles. On the other hand, a more electrophilic Zr center may also increase its binding affinity for the C=C bond within the zirconacycle. X-ray crystal structure analysis of related Ti systems has revealed no  $\pi$ -interaction in Cp<sub>2</sub>Ti[N(c-C<sub>6</sub>H<sub>11</sub>)CH=C(Me)CH(Ph)] but a remarkably strong Ti/ C=C interaction in Cp(Cl)Ti[N(*t*-Bu)CH=C(Me)CH(Ph)], which presumably has a more electrophilic Ti center.<sup>9</sup> If the C=C bond dissociation step indeed precedes electrophilic insertion in the *ansa*bridged Zr system (Scheme 2), the rate at which the zirconacycle unfolds the ring will be critical in determining the efficiency of the overall insertion.

In this paper we report the synthesis and characterization of new zirconocene-1-aza-1,3-diene complexes containing a  $[Me_2Si]$  ansa bridge, their reactivities toward various electrophiles, and comparative kinetic data for ketone insertion into zirconacycles with different ancillary ligands  $(Me_2Si(C_5H_4)_2 \text{ vs} Cp_2, \text{ NPh vs } N(p-MeOC_6H_4))$  and different ketone substrates  $(Ph_2C=O \text{ vs} (p-MeOC_6H_4)_2C=O)$ . We also report the computational studies on the conformational change of zirconocene-1-aza-1,3-diene complexes and its implications for the mechanism of ketone insertion into the zirconacycles.

#### **Results and Discussion**

Synthesis of Zirconocene-1-Aza-1,3-diene Complexes. The Me<sub>2</sub>Si-bridged zirconocene-1-aza-1,3-diene complexes 2a,b were prepared in one-pot syntheses from  $[Me_2Si(C_5H_4)_2]ZrCl_2$ and the corresponding  $\alpha,\beta$ -unsaturated imines, following a procedure developed by Whitby (eq 1).<sup>4</sup> The <sup>1</sup>H NMR and <sup>13</sup>C  $\{^{1}H\}$  NMR spectra of the zirconium products in C<sub>6</sub>D<sub>6</sub> confirmed the formation of Zr–C bonds; the characteristic proton ( $\delta$  1.59 for **2a** and  $\delta$  1.68 for **2b**) and carbon resonances ( $\delta$  69.8 for **2a** and  $\delta$  69.3 for **2b**) are consistent with those for zirconium alkyl species. To fully evaluate the electronic effect of nitrogen substituents on the reactivity of zirconacycles, we attempted to synthesize zirconium complexes with an electron-withdrawing group (CF<sub>3</sub> in 2c and NO<sub>2</sub> in 2d) on the para position of the N-bound aryl ring. Surprisingly, no desired zirconium products were observed under reaction conditions similar to those used for the preparation of 2a,b.

Assuming that zirconacycle 2a has an envelope-shaped structure in solution (regardless of the absence or presence of



a Zr/C=C interaction), one would expect four possible stereoisomers: one pair of enantiomers A with the Ph group adopting the *pseudoequatorial* position and the other pair **B** with the Ph group adopting the *pseudoaxial* position (Figure 1). The <sup>1</sup>H NMR spectrum of 2a in benzene- $d_6$  showed multiple peaks for each of the eight inequivalent Cp hydrogens and two doublets for both PhNCH ( $\delta$  5.90) and ZrCHPh ( $\delta$  1.59) resonances, which are coupled to each other with a long-range coupling constant of  ${}^{4}J_{H-H} = 1.4$  Hz.<sup>10</sup> In a selective homonuclear decoupling <sup>1</sup>H NMR experiment, saturating the ZrCHPh resonance resulted in the disappearance of  ${}^{4}J_{H-H}$  coupling and the PhNCH resonance became one doublet with the olefinic coupling constant of  ${}^{3}J_{H-H} = 6.7$  Hz unchanged (Figure 2). This result implies only one set of resonances observable for the zirconacycle, which could be explained by one of the following three scenarios: (1) the ring-flipping or  $\mathbf{A} \leftrightarrow \mathbf{B}$  interconversion is fast on the NMR time scale and the average of A and B resonances has been observed, (2) the equilibrium mixture of A and B is established, but one pair is highly populated, or (3) there are high kinetic barriers for  $A \leftrightarrow B$  interconversion, and one of the two pairs is kinetically formed during the synthesis. To distinguish these hypotheses experimentally, variabletemperature NMR experiments with 2a were performed, but no dynamic change was observed in the temperature range from -60 to +70 °C.

For the comparison between [Me<sub>2</sub>Si] *ansa*-bridged and bis-Cp systems, zirconocene–1-aza-1,3-diene complexes with two plain Cp ligands were prepared from Negishi's reagent (eq 2).<sup>11</sup> Again, the stability of the zirconacycles was dependent on the nitrogen substituents. Complex **3c**, with an electron-withdrawing CF<sub>3</sub> group, was observed in the crude product along with other unidentified Zr species, but it quickly decomposed during purification. From the more electron-deficient imine **1d**, there was no evidence that the zirconium complex **3d** formed.



X-ray Structures of Zirconocene-1-Aza-1,3-diene Complexes. To further study the zirconocene-1-aza-1,3-diene complexes, X-ray-quality crystals of 2a and 3a,b were grown by



**Figure 2.** Selective homonuclear decoupling <sup>1</sup>H NMR experiment for the complex **2a** in benzene- $d_6$  (the normal <sup>1</sup>H NMR spectrum shown at the bottom and the ZrCHPh proton-decoupled <sup>1</sup>H NMR spectrum shown at the top).



**Figure 3.** ORTEP diagram (50% probability level) of the molecular structure of  $[Me_2Si(C_5H_4)_2]Zr[N(Ph)CH=CHCH(Ph)]$  (**2a**). Selected bond lengths (Å) and angles (deg): Zr-N1 = 2.133(5),  $Zr \cdots C1 = 2.570(7)$ ,  $Zr \cdots C2 = 2.576$  (7), Zr-C3 = 2.320(6), C1-C2 = 1.364(10), C2-C3 = 1.446(10); N1-Zr-C3 = 85.5(2), Zr-N1-C1 = 90.7(4), C1-N1-C4 = 118.5(5), Zr-N1-C4 = 146.1(5), (C3-Zr-N1)-(C3-C2-C1-N1) = 124.6(4).

adding pentane to saturated toluene solutions of the zirconium complexes. Thermal ellipsoid plots of the solid-state structures of 2a and 3a,b are shown in Figures 3-5, respectively, and the crystallographic data are summarized in Table 1. Consistent with the structures of related compounds,<sup>6,12-14</sup> the 1-aza-1,3-diene moiety in all three structures is strongly bent with respect to the N1-Zr-C3 plane. The dihedral angles between the planes defined by N1-C1-C2-C3 and N1-Zr-C3 are 55.4(4), 54.6(2), and 57.2(2)° for 2a and 3a,b, respectively. The throughspace distances for Zr····C1 (2a, 2.570(7) Å; 3a, 2.589(3) Å; **3b**, 2.568(3) Å) and Zr · · · C2 (**2a**, 2.576(7) Å; **3a**, 2.700(3) Å; **3b**, 2.583(3) Å) are much longer than typical Zr–C bonds, although they are relatively close to the sum of Zr and C covalent radii.<sup>15</sup> The short distances for C1-C2 bonds (2a, 1.364(10) Å; **3a**, 1.376(4) Å; **3b**, 1.379(5) Å) confirm that they are C=C bond units and the zirconium complexes are best described as metallacyclopentenes, rather than  $\eta^4$ -1-aza-1,3-



**Figure 4.** ORTEP diagram (50% probability level) of the molecular structure of  $Cp_2Zr[N(Ph)CH=CHCH(Ph)]$  (**3a**). Selected bond lengths (Å) and angles (deg): Zr-N1 = 2.129(2),  $Zr \cdots C1 = 2.589(3)$ ,  $Zr \cdots C2 = 2.700$  (3), Zr-C3 = 2.321(3), C1-C2 = 1.376(4), C2-C3 = 1.452(4); N1-Zr-C3 = 84.79(9), Zr-N1-C1 = 92.25(16), C1-N1-C4 = 118.7(2), Zr-N1-C4 = 143.27(19), (C3-Zr-N1)-(C3-C2-C1-N1) = 125.4(2).



**Figure 5.** ORTEP diagram (50% probability level) of the molecular structure of  $Cp_2Zr[N(p-MeOC_6H_4)CH=CHCH(Ph)]$  (**3b**). Selected bond lengths (Å) and angles (deg): Zr-N1 = 2.129(3),  $Zr \cdots C1 = 2.568(3)$ ,  $Zr \cdots C2 = 2.583(3)$ , Zr-C3 = 2.329(3), C1-C2 = 1.379(5), C2-C3 = 1.460(5); N1-Zr-C3 = 84.33(11), Zr-N1-C1 = 91.57(19), C1-N1-C4 = 118.2(3), Zr-N1-C4 = 143.9(2), (C3-Zr-N1)-(C3-C2-C1-N1) = 122.8(2).

diene complexes or olefin complexes stabilized by imine N-atom

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Table 1. Summary of Crystallographic Data

	2a	3a	3b	5a
empirical formula	C <sub>27</sub> H <sub>27</sub> NSiZr	$C_{25}H_{23}NZr$	C <sub>26</sub> H <sub>25</sub> NOZr	C <sub>38</sub> H <sub>33</sub> NOZr
formula wt	484.81	428.66	458.69	610.87
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\overline{1}$	$P2_1/n$
a, Å	7.7983(1)	11.6487(5)	8.0360(4)	9.3835(1)
b, Å	21.9708(4)	7.8515(4)	11.0923(6)	14.7303(2)
c, Å	13.9755(2)	21.7801(10)	11.5186(6)	20.8409(3)
α. deg	90	90	96.383(1)	90
$\beta$ , deg	104.602(1)	99.606(1)	95.822(1)	95.920(1)
$\gamma$ , deg	90	90	90.250(1)	90
$V, Å^3$	2317.15(6)	1964.07(16)	1014.99(9)	2865.30(6)
Z	4	4	2	4
$d_{\rm calcd}$ , g/cm <sup>3</sup>	1.390	1.450	1.501	1.416
λ. Å	1.54178	0.77490	0.77490	1.54178
$\mu$ , mm <sup>-1</sup>	4.469	0.705	0.693	3.380
no. of data collected	16770	20660	12305	23962
no. of unique data	3401	4970	4964	5145
$R1, wR2 (I > 2\sigma(I))$	0.0662, 0.1582	0.0477, 0.1208	0.0477, 0.1442	0.0250, 0.0654
R1, wR2 (all data)	0.0897, 0.1747	0.0543, 0.1245	0.0507, 0.1469	0.0275, 0.0669





coordination.<sup>16</sup> It should also be noted that, in the solid state, all three zirconium complexes prefer the conformation with the Ph group occupying the pseudoequatorial position.

2.160

2.254

57.1

124.5

0.8

3f

2.248

The [Me<sub>2</sub>Si] bridge is expected to exert some influence on the structures of the zirconacycles, which can ultimately affect the reactivities of these zirconium complexes. The geometrical data for the ansa complex 2a and bis-Cp complexes, including the two known compounds  $3e^6$  and  $3f^{12}$  (Figure 6), are summarized in Table 2. As expected for ansa complexes, the interplanar-ring angle  $\alpha$  for **2a** (61.3°) is larger than those in the bis-Cp system (54.6-57.1°), due to the constraint associated with the natural bond angle preference of the bridging Si atom.<sup>17</sup> The  $Zr-Cp_{cent}$  vector in **2a** deviates further from the Cp ring normal, and the tilt angle  $\gamma$  increases about 1.6–3.0° compared to those for the bis-Cp complexes. These results are consistent with the notion that the zirconium center with an ansa-bridged ligand should be sterically more accessible. Interestingly, the Cp ligand and the N substituent seem to have little effect on the Zr-Cp<sub>cent</sub>, Zr-C3, and Zr-N1 bond distances. However, in complex 3f, the Zr-C3 bond is shortened



**Figure 6.** Zirconocene–1-aza-1,3-diene complexes that have been previously studied by X-ray diffraction.



Figure 7. Calculated energies for the two Zr conformers of 2a and the transition state for ring flipping.

by 0.07 Å, which may be attributed to the effect of the substituent (alkyl vs aryl) on C3. The weaker  $C3-C(sp^3)$  bond in **3f** strengthens the Zr-C3 interaction by providing a carbon orbital with more s orbital character.<sup>18</sup>

**Computational Studies on the Conformational Change of 2a.** Because the variable-temperature NMR experiments offered little information on the solution structure of **2a**, DFT studies were conducted to gain mechanistic insights on the conformational change of the zirconacycle. The calculated structure for conformer **A** agrees well with the X-ray crystal-lographic data of **2a**, and conformer **B** shows similar Zr–C3 and Zr–N1 bond distances (see the Supporting Information for details). The calculated relative free energies suggest that conformer **A** is more stable than conformer **B** by 5.6 kcal/mol at 25 °C (Figure 7). This energy difference translates into an equilibrium constant of  $8.6 \times 10^{-5}$ , disfavoring conformer **B** when equilibrated with conformer **A**.

The calculated transition state for the conformational change contains a flattened five-membered ring with the dihedral angle between the N1-C1-C2-C3 and N1-Zr-C3 planes being 7.7°. The low kinetic barrier<sup>19</sup> (15.8 kcal/mol at 298 K) for ring flipping from conformer **A** establishes a rapid interconversion process on the NMR time scale: the rate constant for  $\mathbf{A} \rightarrow \mathbf{B}$  is estimated to be 16 s<sup>-1</sup>. This result is in accord with our experimental observation of only one set of resonances for the <sup>1</sup>H NMR spectrum of **2a**. Although cooling the sample to low temperature can slow down the interconversion process, conformer **A** is still anticipated to be the predominant species. On the basis of the computed thermodynamic data for  $\mathbf{A} \rightarrow \mathbf{B}$  ( $\Delta H = 5.1$  kcal/mol and  $\Delta S = -1.4$  eu), one would predict that at -60 °C the amount of conformer **B** is too small (0.00029 mol % of all Zr species) to be detected.

<sup>(10)</sup> This four-bond coupling of vinyl and allylic hydrogens was also observed for the complexes  $Cp_2Zr[N(Ar)CH=CHCH(Ph)]$  (Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>, *o*-MeC<sub>6</sub>H<sub>4</sub>).<sup>6</sup>

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**Figure 8.** ORTEP diagram (50% probability level) of the molecular structure of Cp<sub>2</sub>Zr[N(Ph)CH=CHCH(Ph)CPh<sub>2</sub>O] (**5a**). Selected bond lengths (Å) and angles (deg): Zr-N1 = 2.1671(15),  $Zr \cdots C1 = 2.967(2)$ ,  $Zr \cdots C2 = 3.473(2)$ ,  $Zr \cdots C3 = 3.550(2)$ , Zr-O1 = 1.9608(12), C1-C2 = 1.337(3), C2-C3 = 1.506(2), C3-C4 = 1.589(2); N1–Zr–O1 = 96.03(5), Zr–N1–C1 = 110.11(11), C1–N1–C5 = 112.90(15), Zr–N1–C5 = 133.00(12).

Whitby and co-workers have experimentally determined the free energy of activation (11.2 kcal/mol at -31 °C) for the ring flipping of the complex Cp<sub>2</sub>Zr[N(Ph)CH=CHCH<sub>2</sub>] (**3g**),<sup>4</sup> which contains two diastereotopic protons distinguishable at -60 °C. Our calculated  $\Delta G^{\ddagger}$  values for the two isomers of **2a** at -31 °C suggest that conformer **A** is less likely to flip the five-membered ring ( $\Delta G^{\ddagger} = 15.5$  kcal/mol) than **3g**, while conformer **B** inverts the ring more rapidly ( $\Delta G^{\ddagger} = 10.1$  kcal/mol).

**Reactivities of Zirconocene**–1-Aza-1,3-diene Complexes. Like other zirconocene–1-aza-1,3-diene complexes, the *ansa* complexes **2a,b** reacted with ketones such as benzophenone to give the ring-expanded products **4a,b**, respectively (eq 3). The reactions with the bis-Cp complexes **3a,b** gave rise to similar seven-membered zirconacycles. Interestingly, the long-range  $({}^{4}J_{H-H})$  coupling was not observed in any of the insertion products, possibly due to a near-180° torsion angle between the allylic C–H bond and the neighboring vinylic C–H bond.<sup>20</sup> Indeed, the X-ray study of **5a** (Figure 8) reveals a torsion angle of 157.6° in the solid state, which is significantly larger than the same angle in the starting material **3a** (116.1°).



In addition to benzophenone, a number of other electrophiles were tested for insertion into complex 2a (in toluene- $d_8$ ). Acetonitrile, benzonitrile, ethyl acetate, and *tert*-butyl acrylate showed no net reaction even at 100 °C. Allylic bromide, 1,2-epoxy-3-butene, and CO<sub>2</sub> consumed complex 2a quickly at room temperature; however, complicated mixtures of zirconium



**Figure 9.** Plots of  $k_{obs}$  versus [PhCOPh] for C=O insertion into Zr-C bonds at 333 K: (**II**) **2a**; (**O**) **2b**; (**II**) **3a**; (**A**) **3b**.



**Figure 10.** Eyring plot for the reaction between 2a and PhCOPh in toluene- $d_8$ .

species as well as the free imine ligand **1a** were observed. Acetic anhydride and CO did not react with **2a** at room temperature but gave intractable products when heated to 100 °C. Acid chlorides such as *p*-toluoyl chloride cleanly converted **2a** into  $[Me_2Si(C_5H_4)_2]ZrCl_2$  at 80 °C, although the fate of the organic moiety could not be determined. Less polar substrates, including ethyl vinyl ether, styrene, and diphenylacetylene, were completely unreactive with **2a** at 100 °C.

Kinetic Studies on Ketone Insertion into Zirconocene-1-Aza-1,3-diene Complexes. For a detailed evaluation of ancillary ligand and ketone substituent effects on the rate of ketone insertion, a series of kinetic studies were conducted. When the zirconium complex 2a was treated with a large excess of PhCOPh (10 equiv) in toluene- $d_8$  at 60 °C, the C=O insertion product formed with no intermediate observed by <sup>1</sup>H NMR spectroscopy. Monitoring the disappearance of 2a gave the pseudo-first-order rate constant  $k_{obs}$  (see the Supporting Information). Variation of PhCOPh concentration (Table S-1 (Supporting Information), Figure 9) indicated that  $k_{obs}$  was linear with PhCOPh concentration, implying that the insertion reaction is second order overall. Zirconium complexes 2b and 3a,b exhibited similar kinetic behavior. Rate measurements for complex 2a between 55 and 75 °C (Figure 10) gave activation parameters  $\Delta H^{\ddagger} = 16.5 \pm 1.2$  kcal/mol and  $\Delta S^{\ddagger} = -22.5 \pm$ 3.4 eu. The negative entropy of activation is consistent with a highly ordered transition state for C=O insertion.

Direct comparison of the second-order rate constants confirms that ansa complexes insert ketones more quickly than bis-Cp complexes. With the same imine ligand, complex 2a is about 2.8 times more reactive than the bis-Cp complex 3a. The rate enhancement is less pronounced with an electron-rich imine ligand; the ansa complex 2b is only about 1.8 times more reactive than 3b. On the other hand, the property of the imine ligand also plays a key role in controlling the reactivity of the zirconium complexes. Adding a *p*-methoxy group to the N-bound aryl ring decreases the insertion rate constant by 2.8 in the bis-Cp case and by 4.2 in the [Me<sub>2</sub>Si] bridge case. The steric effect is expected to be minimal, as the methoxy group is not in the close proximity of the Zr center and there are essentially no structural differences between 3a and 3b. Instead, the electronic effect dominates and our kinetic data suggest that an electron-deficient Zr center is more favorable for the ketone insertion reactions. These results, in return, provide indirect evidence that the  $[Me_2Si(C_5H_4)_2]$ -ligated Zr center is more electron deficient than the  $Cp_2$ -ligated Zr center.<sup>17a,21</sup>

The kinetics for the insertion reaction with 2a was further explored using 4,4'-dimethoxybenzophenone as the ketone substrate (see the Supporting Information for details). The second-order rate constant obtained at 60 °C is approximately 2.2 times greater than the rate constant for the unsubstituted benzophenone, which should contain a more electrophilic carbonyl carbon. The difference in reactivity observed for different ketone substrates does, however, correlate with the basicity of the carbonyl oxygen.

Mechanism of Ketone Insertion into Zr–C Bonds of Zirconocene–1-Aza-1,3-diene Complexes. The mechanism of alkene insertion into group IV metal–carbon bonds has been extensively studied, due to its importance in metallocene-catalyzed alkene polymerization.<sup>22</sup> It is generally accepted that the insertion reactions occur by a two-step process involving



initial  $\eta^2$  coordination of the alkene and then alkyl migration to construct the C-C bond. In contrast, mechanistic information on the insertion of aldehydes and ketones into similar metal-carbon bonds is limited, despite its high relevance in many catalytic and stoichiometric reactions.<sup>23,24</sup> For the ketone insertion into zirconocene-1-aza-1,3-diene complexes, it is conceivable that an insertion reaction takes place following a similar ketone coordination-alkyl migration sequence. Although both zirconocene $-\eta^2$ -ketone<sup>24f,25</sup> and zirconocene $-\eta^1$ -ketone complexes<sup>26</sup> are known in the literature,<sup>27</sup> the absence of electrons at the d<sup>0</sup> metal in our zirconocene-1-aza-1,3-diene complexes prevents stabilization of  $\eta^2$ -ketone complexes by back-bonding, particularly from the lateral coordination site. Inspecting the space-filling model of these complexes also suggests that severe steric repulsion can be anticipated if the ketone substrate does adopt the  $\eta^2$  coordination mode prior to insertion. For these reasons, the mechanism for the ketone insertion in this case is more likely to involve initial  $\eta^1$ coordination of the ketone, followed by C-C bond formation (Scheme 3).<sup>28</sup> The fact that ethyl vinyl ether, styrene, and diphenylacetylene do not react with 2a further supports this

<sup>(15)</sup> For covalent radius data of Zr ( $1.75 \pm 0.07$  Å) and C (C(sp<sup>3</sup>), 0.76  $\pm$  0.01 Å; C(sp<sup>2</sup>), 0.73  $\pm$  0.02 Å), see: Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

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<sup>(18)</sup> The C2–C3–alkyl angle in **3f** is 112.0°, while the C2–C3–Ph angle in **3a** is 121.3°.

<sup>(19)</sup> Calculated activation parameters for  $\mathbf{A} \rightarrow \mathbf{B}$ :  $\Delta H^{\ddagger} = 14.3$  kcal/ mol and  $\Delta S^{\ddagger} = -5.0$  eu.

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<sup>(28)</sup> We cannot rule out a concerted mechanism where ketone activation and C–C bond formation take place simultaneously in the transition state, but the Zr/O interaction should play a major role.

mechanistic hypothesis, as C=C and C=C bonds lack the ability to coordinate to Zr in an end-on fashion. In view of the observed second-order kinetics for the ketone insertion, the coordination step is proposed to be the rate-determining step, which is consistent with our experimental results that reactions are favored by more electron-deficient metal centers as well as more basic ketone substrates.

#### Conclusions

A new class of zirconocene-1-aza-1,3-diene complexes with a [Me<sub>2</sub>Si] *ansa* bridge has been synthesized. Kinetic studies on the reactions between benzophenone and these zirconocene complexes, including their bis-Cp equivalents, demonstrate that the incorporation of a [Me<sub>2</sub>Si] *ansa* bridge reduces the kinetic barrier for insertion. The reactions are faster when a more basic ketone is used but are slower when a more electron-rich substituent is introduced to the imine nitrogen. The kinetic data in combination with other reactivity studies support a two-step process for the overall insertion: initial coordination of the ketone in an  $\eta^1$  fashion followed by formation of the C-C bond. Ring flipping of the zirconacycles, which has been studied by DFT calculations, is too fast to affect the insertion reactions.

#### **Experimental Section**

**General Comments.** All air-sensitive compounds were prepared and handled under an argon atmosphere using standard Schlenk and inert-atmosphere box techniques. Toluene and THF were deoxygenated and dried over an Innovative Technology solvent purification system. Toluene- $d_8$  and benzene- $d_6$  were distilled from Na and benzophenone under an argon atmosphere. CD<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub>, degassed by three freeze-pump-thaw cycles, and then purified by vacuum transfer at room temperature. [Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]ZrCl<sub>2</sub><sup>21b</sup> and  $\alpha,\beta$ -unsaturated imines (1a-d)<sup>29</sup> were prepared as described in the literature.

[Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]Zr[N(Ph)CH=CHCH(Ph)] (2a). Under an argon atmosphere n-BuLi (0.69 mL, 1.6 M in hexanes, 1.10 mmol) was added dropwise to a solution of [Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]ZrCl<sub>2</sub> (174 mg, 0.50 mmol) in THF (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h before a solution of 1a (104 mg, 0.50 mmol) in THF (10 mL) was added via cannula. The resulting mixture was then slowly warmed to room temperature over a period of 5 h and stirred for an additional 1 h, at which time a bright orange solution formed. The volatiles were removed under vacuum, and the residue was treated with toluene and filtered under argon. Removal of toluene under vacuum afforded the crude product, which was subjected to recrystallization in toluene/pentane to give 2a as an orange solid (170 mg, 70%) yield). <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ,  $\delta$ ): 7.32–7.26 and 7.04-6.94 (m, Ph, 10H), 6.28-6.26 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.17-6.15 (m, C<sub>5</sub> $H_4$ , 1H), 5.90 (dd,  ${}^{3}J_{H-H} = 6.7$  Hz,  ${}^{4}J_{H-H} = 1.4$  Hz, NCH=CHCH, 1H), 5.67-5.65 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 5.54-5.52 (m,  $C_5H_4$ , 1H), 5.46–5.41 (m, NCH=CHCH and  $C_5H_4$ , 3H), 5.07-5.05 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 4.62-4.60 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 1.59 (dd,  ${}^{3}J_{H-H} = 9.2$  Hz,  ${}^{4}J_{H-H} = 1.4$  Hz, NCH=CHCH, 1H), 0.44 (s, SiCH<sub>3</sub>, 3H), 0.01 (s, SiCH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, benzene- $d_6$ ,  $\delta$ ): 152.00, 146.77, 129.00, 128.67, 128.44, 127.92, 127.68, 127.33, 122.63, 122.24, 121.17, 119.11, 117.63, 114.55, 111.36, 109.65, 108.97, 107.37, 106.62, 105.79, 104.61, 102.33, 100.81, 69.78 (NCH=CHCH), -4.65 (SiCH<sub>3</sub>), -6.60 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>27</sub>H<sub>27</sub>NSiZr: C, 66.89; H, 5.61; N, 2.89. Found: C, 66.94; H, 5.68; N, 2.76.

[Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]Zr[N(p-MeOC<sub>6</sub>H<sub>4</sub>)CH=CHCH(Ph)] (2b). This compound was prepared in 78% yield by a procedure similar to that used for **2a**. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.31–6.83 (m, Ph, 9H), 6.42-6.41 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.22-6.20 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.09 (dd,  ${}^{3}J_{H-H} = 6.6$  Hz,  ${}^{4}J_{H-H} = 1.4$  Hz, NCH=CHCH, 1H), 5.92-5.90 (m,  $C_5H_4$ , 1H), 5.89-5.87 (m,  $C_5H_4$ , 1H), 5.86–5.84 (m, C<sub>5</sub> $H_4$ , 1H), 5.64 (dd,  ${}^{3}J_{H-H} = 9.2$  and 6.6 Hz, NCH=CHCH, 1H), 5.53-5.52 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 5.35-5.34 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 4.64–4.62 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 3.82 (s, OCH<sub>3</sub>, 3H), 1.50  $(dd, {}^{3}J_{H-H} = 9.2 \text{ Hz}, {}^{4}J_{H-H} = 1.4 \text{ Hz}, \text{ NCH}=CHCH, 1H), 0.78$ (s, SiCH<sub>3</sub>, 3H), 0.39 (s, SiCH<sub>3</sub>, 3H). <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>, δ): 7.24-7.04 (m, Ph, 9H), 6.39-6.38 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.32–6.30 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.09 (dd,  ${}^{3}J_{H-H} = 6.5$  Hz,  ${}^{4}J_{H-H}$ = 1.1 Hz, NCH = CHCH, 1H), 5.79-5.77 (m,  $C_5H_4$ , 1H), 5.68-5.66 (m,  $C_5H_4$ , 1H), 5.60-5.52 (m,  $C_5H_4$  and NCH=CHCH, 3H), 5.21-5.19 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 4.76-4.74 (m,  $C_5H_4$ , 1H), 3.55 (s, OCH<sub>3</sub>, 3H), 1.68 (dd,  ${}^{3}J_{H-H} = 9.2$  Hz,  ${}^{4}J_{H-H}$ = 1.1 Hz, NCH=CHCH, 1H), 0.58 (s, SiCH<sub>3</sub>, 3H), 0.14 (s, SiCH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 155.47, 146.53, 145.48, 128.40, 122.41, 121.79, 121.52, 120.09, 117.36, 114.14, 114.00, 111.07, 109.42, 108.44, 106.88, 106.36, 105.79, 103.20, 102.25, 100.93, 69.30 (NCH=CHCH), 55.53 (OCH<sub>3</sub>), -4.50 (SiCH<sub>3</sub>), -6.27 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>28</sub>H<sub>29</sub>NOSiZr: C, 65.32; H, 5.68; N, 2.72. Found: C, 65.07; H, 5.82; N, 2.68.

**Cp<sub>2</sub>Zr[N(Ph)CH=CHCH(Ph)] (3a).** The synthesis of this complex has been previously reported with limited characterization data.<sup>4</sup> It was prepared in 73% yield by a procedure similar to that used for **2a**. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.34–6.92 (m, *Ph*, 10H), 6.09 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, NCH=CHCH, 1H), 6.05 (s, *Cp*, 5H), 5.68 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 and 6.7 Hz, NCH=CHCH, 1H), 5.51 (s, *Cp*, 5H), 1.57 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, NCH=CHCH, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 152.16, 147.34, 128.64, 128.48, 122.97, 121.93, 121.84, 121.76, 119.90, 107.23, 104.72, 103.83, 68.37 (NCH=CHCH). Anal. Calcd for C<sub>25</sub>H<sub>23</sub>NZr: C, 70.04; H, 5.41; N, 3.27. Found: C, 69.93; H, 5.41; N, 3.25.

**Cp<sub>2</sub>Zr[N(***p***-MeOC<sub>6</sub>H<sub>4</sub>)CH=CHCH(Ph)] (3b).** This compound was prepared in 85% yield by a procedure similar to that used for **2a**. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.32–6.84 (m, *Ph*, 9H), 6.08 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.2 Hz, NCH=CHCH, 1H), 6.01 (s, *Cp*, 5H), 5.62 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 and 6.6 Hz, NCH=CHCH, 1H), 5.49 (s, *Cp*, 5H), 3.83 (s, OCH<sub>3</sub>, 3H), 1.49 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.2 Hz, NCH=CHCH, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 155.57, 147.52, 146.07, 128.46, 122.96, 122.46, 121.74, 120.71, 113.94, 107.03, 103.93, 103.61, 68.12 (NCH=CHCH), 55.55 (OCH<sub>3</sub>). Anal. Calcd for C<sub>26</sub>H<sub>25</sub>NOZr: C, 68.08; H, 5.49; N, 3.05. Found: C, 68.02; H, 5.48; N, 3.06.

**Cp<sub>2</sub>Zr[N(***p***-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)CH=CHCH(Ph)] (3c).** This compound was detected from the crude product by following a procedure similar to that used for **2a**; however, attempted recrystallization in toluene/pentane led to the decomposition of the zirconium complex. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.57–6.96 (m, *Ph*, 9H), 6.08 (s, *Cp*, 5H), 6.03 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, NCH=CHCH, 1H), 5.78 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 and 6.8 Hz, NCH=CHCH, 1H), 5.54 (s, *Cp*, 5H), 1.70 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.2 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, NCH=CHCH, 1H).

[Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]Zr[N(Ph)CH=CHCH(Ph)CPh<sub>2</sub>O] (4a). Under an argon atmosphere, benzophenone (115 mg, 0.63 mmol) was added to a solution of 2a (305 mg, 0.63 mmol) in toluene (30 mL). The resulting mixture was stirred at 80 °C for 8 h, cooled to room temperature, and passed through a short plug of dry Celite under argon. The solvent was removed under vacuum and the residue was subjected to recrystallization in toluene/pentane to give 4a as a light yellow solid (365 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ,  $\delta$ ): 7.77–6.75 (m, *Ph* and C<sub>5</sub>H<sub>4</sub>, 23H), 6.21–6.15 (m, C<sub>5</sub>H<sub>4</sub> and NCH=CHCH, 3H), 6.02–5.99 (m,

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C<sub>5</sub>*H*<sub>4</sub>, 1H), 5.84 (br s, C<sub>5</sub>*H*<sub>4</sub>, 1H), 5.73–5.71 (m, C<sub>5</sub>*H*<sub>4</sub>, 1H), 5.40 (dd,  ${}^{3}J_{H-H} = 9.5$  and 7.8 Hz, NCH=CHCH, 1H), 4.13 (d,  ${}^{3}J_{H-H} = 9.5$  Hz, NCH=CHCH, 1H), 0.62 (s, SiCH<sub>3</sub>, 3H), 0.44 (s, SiCH<sub>3</sub>, 3H).  ${}^{13}C{}^{1}H$ } NMR (101 MHz, toluene-*d*<sub>8</sub>,  $\delta$ ): 156.21, 148.61, 146.85, 142.37, 136.88, 136.82, 130.45, 129.49, 129.32, 127.24, 126.82, 126.73, 126.54, 125.97, 122.58, 121.29, 120.39, 117.11, 114.88, 112.97, 112.39, 110.77, 109.65, 109.08, 99.54, 57.26 (NCH=CHCH), -3.84 (SiCH<sub>3</sub>), -6.71 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>37</sub>NOZrSi: C, 72.02; H, 5.59; N, 2.10. Found: C, 72.13; H, 5.37; N, 2.17.

 $[Me_{2}Si(C_{5}H_{4})_{2}]Zr[N(p-MeOC_{6}H_{4})CH=CHCH(Ph)CPh_{2}O] (4b).$ This compound was prepared in 88% yield by a procedure similar to that used for 4a. <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ,  $\delta$ ): 7.83-6.83 (m, Ph and  $C_5H_4$ , 21H), 6.73-6.71 (m,  $C_5H_4$ , 1H), 6.22-6.20 (m, C<sub>5</sub>H<sub>4</sub> and NCH=CHCH, 2H), 6.14-6.12 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.06-6.05 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 5.84 (br s, C<sub>5</sub>H<sub>4</sub>, 1H), 5.79–5.77 (m, C<sub>5</sub> $H_4$ , 1H), 5.41 (dd,  ${}^{3}J_{H-H} = 9.5$  and 9.4 Hz, NCH=CHCH, 1H), 4.17 (d,  ${}^{3}J_{H-H} = 9.4$  Hz, NCH=CHCH, 1H), 3.55 (s, OCH<sub>3</sub>, 3H), 0.65 (s, SiCH<sub>3</sub>, 3H), 0.48 (s, SiCH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, toluene- $d_8$ ,  $\delta$ ): 154.83, 149.50, 148.81, 147.00, 142.61, 138.04, 136.88, 136.82, 130.47, 129.29, 129.20, 127.24, 126.74, 126.68, 126.60, 125.90, 121.46, 116.23, 115.54, 113.72, 113.32, 112.06, 111.30, 109.74, 109.53, 100.11, 57.24 (NCH=CHCH), 54.68 (OCH<sub>3</sub>), -3.98 (SiCH<sub>3</sub>), -6.52 (SiCH<sub>3</sub>). No satisfactory elemental analysis results were obtained for this compound, despite repeated crystallizations to purify the product. Anal. Calcd for C<sub>41</sub>H<sub>39</sub>NO<sub>2</sub>ZrSi: C, 70.65; H, 5.64; N, 2.01. Found: C, 69.92; H, 5.17; N, 2.13.

**Cp<sub>2</sub>Zr[N(Ph)CH=CHCH(Ph)CPh<sub>2</sub>O] (5a).** This compound was prepared in 91% yield by a procedure similar to that used for **4a**. X-ray-quality crystals of **5a** were grown by adding pentane to a saturated toluene solution of the zirconium complex. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.57–6.59 (m, *Ph*, 20H), 6.51 (s, *Cp*, 5H), 6.17 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, NCH=CHCH, 1H), 5.96 (s, *Cp*, 5H), 4.91 (t, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, NCH=CHCH, 1H), 3.80 (d, <sup>3</sup>J<sub>H-H</sub> = 9.2 Hz, NCH=CHCH, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 156.12, 147.90, 146.19, 142.47, 138.24, 130.39, 129.44, 129.33, 127.97, 127.83, 127.38, 126.92, 126.75, 126.45, 125.94, 122.16, 121.25, 119.48, 112.12, 111.53, 98.31, 56.75 (NCH=CHCH). Anal. Calcd for C<sub>38</sub>H<sub>33</sub>NOZr: C, 74.71; H, 5.44; N, 2.29. Found: C, 74.51; H, 5.39; N, 2.21.

**Cp<sub>2</sub>Zr[N(***p***-MeOC<sub>6</sub>H<sub>4</sub>)CH=CHCH(Ph)CPh<sub>2</sub>O] (5b).** This compound was prepared in 90% yield by a procedure similar to that used for **4a**. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>,  $\delta$ ): 7.69–6.62 (m, *Ph*, 19H), 6.23 (s, *Cp*, 5H), 6.16 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.5 Hz, NCH=CHCH, 1H), 5.80 (s, *Cp*, 5H), 5.11 (t, <sup>3</sup>*J*<sub>H-H</sub> = 8.4 Hz, NCH=CHCH, 1H), 3.97 (d, <sup>3</sup>*J*<sub>H-H</sub> = 9.2 Hz, NCH=CHCH, 1H), 3.97 (d, <sup>3</sup>*J*<sub>H-H</sub> = 9.2 Hz, NCH=CHCH, 1H), 3.45 (s, OCH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, benzene-*d*<sub>6</sub>,  $\delta$ ): 154.64, 150.12, 148.46, 146.68, 142.79, 138.84, 130.67, 129.76, 129.58, 127.93, 127.69, 127.48, 126.93, 126.68, 126.08, 122.79, 122.44, 113.81, 112.05, 111.21, 99.54, 57.04 (NCH=CHCH), 55.02 (OCH<sub>3</sub>). Anal. Calcd for C<sub>39</sub>H<sub>35</sub>NO<sub>2</sub>Zr: C, 73.08; H, 5.50; N, 2.18. Found: C, 72.79; H, 5.43; N, 2.08.

[Me<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]Zr[N(Ph)CH=CHCH(Ph)C(*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O] (4h). This compound was prepared in 89% yield by a procedure similar to that used for 4a. <sup>1</sup>H NMR (400 MHz, toluene- $d_8$ ,  $\delta$ ): 7.60–6.71 (m, *Ph* and C<sub>5</sub>H<sub>4</sub>, 20H), 6.62–6.60 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 6.13–6.08 (m, C<sub>5</sub>H<sub>4</sub> and NCH=CHCH, 3H), 5.99–5.97 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 5.84 (br s, C<sub>5</sub>H<sub>4</sub>, 1H), 5.65–5.64 (m, C<sub>5</sub>H<sub>4</sub>, 1H), 5.29 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.5 and 9.4 Hz, NCH=CHCH, 1H), 3.99 (d, <sup>3</sup>J<sub>H-H</sub> = 9.4 Hz, NCH=CHCH, 1H), 3.44 (s, OCH<sub>3</sub>, 3H), 3.33 (s, OCH<sub>3</sub>, 3H), 0.58 (s, SiCH<sub>3</sub>, 3H), 0.41 (s, SiCH<sub>3</sub>, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, toluene- $d_8$ ,  $\delta$ ): 158.86, 158.66, 155.95, 142.83, 140.66, 139.08, 130.62, 130.42, 130.40, 128.10, 127.93, 127.08, 125.9, 124.27, 122.41, 121.18, 120.26, 120.11, 117.06, 114.89, 113.09, 112.51, 112.44, 111.94, 110.83, 109.69, 109.15, 98.90, 57.56 (NCH=CHCH), 54.33 (OCH<sub>3</sub>), 54.23 (OCH<sub>3</sub>), -3.84  $(SiCH_3)$ , -6.67  $(SiCH_3)$ . Anal. Calcd for  $C_{42}H_{41}NO_3ZrSi$ : C, 69.38; H, 5.68; N, 1.93. Found: C, 69.00; H, 5.23; N, 2.08.

NMR Measurements of Rate Constants for Ketone Insertion into Zirconocene–1-Aza-1,3-diene Complexes. In a typical experiment, benzophenone or 4,4'-dimethoxybenzophenone (10–60 mg) was dissolved in toluene- $d_8$  (0.5–1 mL) with added toluene (2–5  $\mu$ L) as an internal standard. The resulting solution was transferred into a resealable NMR tube, followed by the addition of the zirconocene–1-aza-1,3-diene complex. The first <sup>1</sup>H NMR spectrum was recorded (on a Bruker AMX 400 MHz NMR spectrometer) within 5 min, and spectra were taken every 10–20 min for 3–5 half-lives. The integration for the higher field MeSi resonances of *ansa* complexes (or the integration for the lower field Cp resonances of bis-Cp complexes) was compared to the integration for the toluene methyl resonance ( $\delta$  2.11). The probe temperature was calibrated using 100% ethylene glycol.<sup>30</sup>

**Computational Details.** DFT calculations on the zirconium complexes were performed by employing the Gaussian 03 program (Revision D.02).<sup>31</sup> The B3LYP gradient corrected exchange hybrid DFT method<sup>32</sup> was applied. Geometry optimizations were performed in the gas phase using the default convergence criteria without any constraints. The LANL2DZ ECP basis set was used for the zirconium atom,<sup>33</sup> while the allelectron 6-31G(d) Pople basis set was employed for H, C, N, and Si atoms.<sup>34</sup> Frequency calculations were employed to characterize the stationary points as minima or transition-state structures, as well as to determine zero-point energies (ZPEs) for free-energy calculations at 298.15 K and 1 atm. The Cartesian coordinates of the optimized structures and the corresponding thermodynamic data are summarized in the Supporting Information.

X-ray Structure Determinations. Crystal data collection and refinement parameters are summarized in Table 1. For complexes 3a,b, data were collected on a Bruker APEX2 CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to  $\lambda = 0.77490$  Å. For complexes **2a** and **5a**, data were collected at 150 K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The data frames were collected using either APEX2 or SMART and integrated using SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections on the basis of the multiscan technique used in SADABS. The structures were solved by a combination of direct methods in SHELXTL and difference Fourier techniques and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters.

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The H atoms were either located or calculated and subsequently treated with a riding model. For complex **2a**, high-resolution data were very weak, which was also indicated by the higher value of  $R_{\rm int}$  (not diffracting very well, beginning at approximately 1 Å). Data used in the refinement were truncated at 0.89 Å resolution.

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**Supporting Information Available:** Figures, tables, and CIF files giving complete details of the crystallographic study, DFT computational results, kinetic data, and plots of these data. This material is available free of charge via the Internet at http://pubs. acs.org.

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